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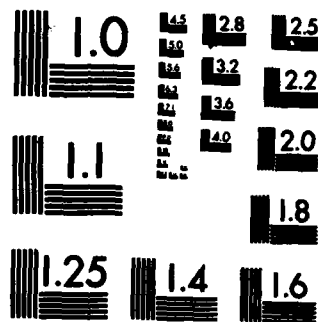
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Luminescent Properties of Graded Cadmium Sulfoselenide Electrodes  
Prepared from Cadmium Sulfide Substrates

by

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Prepared for Publication

in

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dominated by edge emission characteristic of the near-surface  $\text{CdS}_x\text{Se}_{1-x}$  compositions (650-700 nm). The narrowness of the spectra compared to spectra reported for CdSe/S graded solids prepared by diffusion of S into n-CdSe is rationalized in terms of the electronic structures of the two compounds. A previously established linear correlation between emission maxima (nm) and composition in homogeneous  $\text{CdS}_x\text{Se}_{1-x}$  samples provides a spatial probe of electron-hole pair recombination in the inhomogeneous material: Regions from which PL and EL originate can be inferred from their spectral distribution in combination with the AES/depth profile data. The CdS/Se samples can be used as photoanodes of photoelectrochemical cells (PEC's) employing aqueous (poly)sulfide electrolyte. PL quenching accompanying the passage of photocurrent indicates that the effective electric field (EEF) in the solid at -0.3 V vs. SCE extends ~0.1-0.2  $\mu\text{m}$  into the solid. By etching away the graded layer from one face of the CdS/Se crystal, PL can be excited and viewed through the exposed CdS face and yields a similar value for the EEF thickness; photoaction spectra support the PL data in identifying the near-surface portion of the graded zone as principally responsible for photocurrent. Both CdS/Se and CdSe/S electrodes lend themselves to the construction of display devices by spatially-controlled etching: by appropriate masking and etching techniques, patterned, multi-colored emitting electrodes can be fabricated. For the CdS/Se samples, PEC etching can be exploited to control etching depth with excitation wavelength.

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Conversion of optical energy to electricity by photoelectrochemical cells (PEC's) requires the separation of electron-hole ( $e^-h^+$ ) pairs photogenerated in a semiconductor electrode [1-4]. Competing with this separation which yields photocurrent are radiative and nonradiative recombination. Interest in using luminescence as a probe of recombination in PEC's led us to study, among other systems, the emissive properties of homogeneous  $n\text{-CdS}_x\text{Se}_{1-x}$  ( $0 \leq x \leq 1$ ) semiconductor electrodes in photoelectrochemical systems [5,6].

More recently, we have become interested in inhomogeneous  $n\text{-CdS}_x\text{Se}_{1-x}$  semiconductor electrodes which have a band gap gradient perpendicular to the electrode surface. Luminescence from such samples is color-coded to yield information concerning the depth at which recombination occurs. When used in a PEC, such samples provide a spatial probe of the effective electric field (EEF) responsible for  $e^-h^+$  pair separation [7,8].

Graded band gap cadmium sulfoselenide electrodes have been used thus far because the entire range of  $\text{CdS}_x\text{Se}_{1-x}$  compositions ( $0 \leq x \leq 1$ ) is accessible in a single structural type (wurtzite); importantly, the associated bandgaps are all direct and vary smoothly with  $x$  [9]. We have reported previously on electrode materials made by diffusing sulfur into a CdSe substrate to give a thin graded region ( $< 2 \mu\text{m}$ ) with  $x \sim 1$  at the electrode surface [7,8]. Electrodes of this type will be designated in this paper as "CdSe/S".

The photoluminescence (PL) from CdSe/S electrodes consists of a broad spectral band spanning  $\sim 500\text{-}750 \text{ nm}$  which corresponds to band edge emission from the various  $n\text{-CdS}_x\text{Se}_{1-x}$  compositions comprising the graded region. A depth profile of the solid, obtained from Auger electron spectroscopy (AES)/ $\text{Ar}^+$  sputter etching, can be used in conjunction with PL to provide a crude map of the EEF in the graded electrode: PL at a particular wavelength can be correlated with  $e^-h^+$  pair recombination at a specific depth from the electrode surface, and PL from compositions within the EEF is perturbed when the solids are used as PEC electrodes [7,8].

Of related interest is the electroluminescence (EL) of CdSe/S electrodes. When placed in aqueous  $\text{OH}^-/\text{S}_2\text{O}_8^{2-}$  electrolyte, CdSe/S electrodes possessing  $\sim 1\text{-}\mu\text{m}$  thick graded regions yield potential-dependent spectral distributions [8]. In particular, with a 300-mV variation in initiation potential, the color of EL can be shifted reversibly from red to green, corresponding to a significant shift in the spatial distribution of  $\text{e}^- \text{-} \text{h}^+$  pair recombination. This effect, coupled with prospects for fabricating patterned, multi-colored emitting electrodes by controlled etching of the graded layer, may be of interest with regard to display device technology [10].

An intriguing counterpart to the CdSe/S system is a material wherein the direction of the band gap gradient is reversed. We report herein on the luminescent properties of such an electrode which consists of an  $\sim 1\text{-}\mu\text{m}$  thick graded layer of  $\text{n-CdS}_x\text{Se}_{1-x}$  on a CdS substrate. Like its CdSe/S counterpart, this material, CdS/Se, provides spatial information on the origin of  $\text{e}^- \text{-} \text{h}^+$  pair recombination. Comparisons of PL and EL from the two graded electrodes highlight their different electronic structures. In sections below, we describe the synthesis and composition of CdS/Se electrodes, their PL properties in air and as PEC electrodes, and their EL properties. The final section of the paper discusses possible display device applications of these materials.

#### Synthesis and Composition.

As reported previously, synthesis of CdS/Se samples could be achieved by vapor-phase diffusion of Se into single-crystal n-CdS [11-14]; the initially yellow CdS became deep-red to black after this reaction and was a poor electrical conductor. In order to restore sufficient conductivity to permit the CdS/Se samples to serve as PEC electrodes, the solids were subsequently heated with Cd metal [7,8]. The net effect of the synthesis was to yield samples with a thin skin of  $\text{CdS}_x\text{Se}_{1-x}$  compositions with the most Se-rich composition

at the surface. While the crystallinity of the graded material is difficult to assess, previous work provides evidence that some degree of crystallinity is retained as chalcogen substitution occurs in the lattice [7]. The thickness of the skin reflects diffusion processes associated with Se/S lattice substitution and can be controlled by variations in heating time, temperature and pressure. We report herein on samples synthesized by heating CdS with Se at 700°C for 15 min, followed by heat-treatment with Cd for 30 min, also at 700°C.

The technique of AES/Ar<sup>+</sup> sputter etching was used to construct compositional depth profiles for a number of CdS/Se samples. Representative data, pictured in Fig. 1, illustrate the AES signals for Cd, S, and Se as sputter etching proceeds at a rate of ~300 Å/min. The figure indicates that from a near-surface composition of ~CdS<sub>0.15</sub>Se<sub>0.85</sub>, the Se content monotonically declines over a distance of ~0.9 μm (~30 min of sputtering) until the CdS substrate composition is observed. Lattice substitution of Se for S is evidenced by the AES data: At any of the sputter times of Fig. 1, the fractional S and Se compositions sum to ~1.0 when each is expressed as a fraction of its maximum AES signal (the Se signal at t = 0 is treated as 0.85 of its maximum value). In general, surface compositions with x~0.15-0.25 and graded zones with thicknesses of ~0.7-0.9 μm are observed from AES data.

An independent method for estimating the thickness of the graded zone exploited changes in PL properties with chemical etching. The surface of a sample was partially masked and etched until PL characteristic of the substrate was seen. After removal of the mask, a contacting stylus was used to determine the height of the resulting step. Step heights were in rough agreement with AES/sputter etch data.



### PL Properties

Homogeneous crystals of  $\text{CdS}_x\text{Se}_{1-x}$  composition show room temperature band edge PL as a relatively sharp emission peak (fwhm  $\sim 0.05$ - $0.08$  eV) whose wavelength at the emission maximum,  $\lambda_{\text{max}}$ , varies linearly with  $x$ , according to eq. (1) [6, 15].

$$\lambda_{\text{max}} (\text{nm}) = 718 - 210 x \quad (1)$$

The PL spectrum of a typical, freshly prepared CdS/Se sample is shown as curve 1 in Fig. 2. With  $\lambda_{\text{max}}$  at  $\sim 655$  nm (1.89 eV) and a fwhm value of  $\sim 40$  nm (0.12 eV), the PL band appears to owe its existence to edge emission from the near-surface, Se-rich  $\text{CdS}_x\text{Se}_{1-x}$  compositions. Support for this assignment comes from chemical etching. Curves 2-4 of Fig. 2 are PL spectra taken under similar excitation conditions after successive etchings of the graded sample. Particularly noteworthy is the progressive blue shift with etching of  $\lambda_{\text{max}}$  and of the long wavelength PL onset, consistent with the loss of Se-rich compositions. Eventually, the PL spectrum of the CdS substrate is observed (curve 4).

The domination of the Fig. 2 spectra by emission from near-surface compositions is reasonable, since the 457.9-nm light used for excitation is strongly absorbed by  $\text{CdS}_x\text{Se}_{1-x}$  compositions ( $\alpha \sim 10^5 \text{ cm}^{-1}$ ) and penetrates only a small portion of the crystal [16, 17]. Such spectra are, however, very different from those reported for CdSe/S samples with graded regions of comparable thickness [8]. Though the penetration depth of the exciting light is similar for the two materials, the bandwidth of the PL spectrum from CdSe/S is much larger, encompassing emission from throughout the graded region ( $\sim 500$ - $750$  nm), whereas CdS/Se samples show emission primarily from the portion of the graded layer which is directly excited. We suspect that the large difference in spectral characteristics between these

materials hinges on their relative graded-gap structures. Specifically, for CdS/Se, the presence of the smallest band gap material at the surface disfavors  $h^+$  transport toward the bulk along an intrinsic valence band edge gradient as well as excited-state energy transfer, processes which may occur in CdSe/S.

An interesting feature afforded by the CdS/Se system is two-sided excitation and viewing of the graded zone. By etching away the graded layer from one face of a CdS/Se crystal, "backside" illumination with photons having energy between the band gap energies of CdS and CdSe ( $\sim 2.4$  and  $1.7$  eV, respectively [16, 17]) is possible; in this experiment, incident light passes through the CdS substrate and will begin to be absorbed when its energy is roughly matched by the band gap of the corresponding  $\text{CdS}_x\text{Se}_{1-x}$  composition in the graded zone. Additionally, photons which are emitted with energies  $\leq 2.4$  eV can now be viewed from the CdS side. Two-sided viewing provides a method for gauging self-absorption effects in PL spectra obtained, as was Fig. 2, with "frontside" illumination; in "frontside" viewing, emitted light is partially absorbed as it passes through progressively smaller band gap compositions before detection. For the CdS/Se samples of this study, PL spectra obtained with "frontside" 457.9-nm excitation were virtually identical when viewed from the two crystal faces, indicating minimal self-absorption effects.

Complicating a detailed analysis of the PL features of CdS/Se samples are questions related to lateral homogeneity and other emissive transitions. Using a masked laser beam for excitation ( $\sim 0.1 \times 2.0$  mm), PL spectra from various regions of the sample surface were recorded; their similarity indicated good but not perfect homogeneity. With regard to the spectral distribution itself, we often see PL signals at  $\lambda > 750$  nm after heat treatment of CdS with Se. We are uncertain as to the origin of the emission and generally employed samples with minimal PL intensity in this spectral region.

### PL Properties in a PEC.

As with homogeneous  $\text{CdS}_x\text{Se}_{1-x}$  [5,6] and graded  $\text{CdSe/S}$  [7,8] samples,  $\text{CdS/Se}$  platelets can be used as photoelectrodes in PEC's employing aqueous (poly)-chalcogenide electrolytes. Our studies were conducted in  $1\text{M OH}^-/1\text{M S}^{2-}/0.01\text{M S}$  solution to minimize light absorption by the electrolyte. Reasonable short-term stability of the electrodes over the course of PEC experiments was evidenced by the absence of PL spectral shifts which would accompany significant dissolution of the graded layer; lattice exchange of S for Se is well-documented in such experiments [18] and the absence of a PL effect may indicate that the emissive probe is not sufficiently surface-sensitive to detect an altered surface [5]. Most experiments were conducted with edge-mounted crystals to permit two-sided excitation and viewing (vide supra); in this configuration, the CdS side was coated with a transparent, insulating polymer to preclude charge transfer with the electrolyte while permitting optical studies through this face.

In initial studies, photocurrent as a function of excitation wavelength (normalized to a common photon flux) was measured at a potential near short circuit. Both "frontside" and "backside" photoaction spectra were obtained, as shown in Fig. 3. The former, represented by the dashed line in the figure, increases with photon energy beginning at  $\sim 700$  nm. The onset roughly corresponds to the band gap of the surface  $\text{CdS}_{0.2}\text{Se}_{0.8}$  composition, as expected. With shorter wavelengths, a larger fraction of incident light will be absorbed in the near-surface region containing the EEF, leading to the observed larger photocurrent quantum yields. "Backside" excitation produces a photoaction spectrum with a maximum at  $\sim 645$  nm, shown as the solid curve in Fig. 3. This curve provides evidence that the EEF extends only partially into the graded zone: For excitation wavelengths  $\geq 670$  nm, the match of "backside" and "frontside" photoaction spectra suggests that light incident on both faces is absorbed in roughly the same region of the electrode; below 670 nm, the progressive divergence of the two curves suggests that an

increasing fraction of light used for "backside" illumination is absorbed farther from the  $\text{CdS}_{0.2}\text{Se}_{0.8}$  surface in regions of the graded zone characterized by progressively weaker EEF's.

Support for this interpretation comes from PL data. Figure 4 presents PL spectra of a CdS/Se electrode obtained with "frontside" excitation (457.9 nm) and viewing at open circuit and -0.3 V vs. SCE; the inset in the figure reveals that the latter potential corresponds to passage of anodic photocurrent. Typical maximum photocurrent quantum yields for this system are  $\sim 0.25$ . The key feature of the figure is the quenching of PL observed with applied bias. Such quenching is anticipated when  $e^-h^+$  pairs are diverted from recombination to separation by an EEF consisting, in this case, of contributions from band-edge and effective-mass gradients as well as from space-charge formation and applied voltage. The complexity of the CdS/Se electronic structure precludes the quantitative analysis of PL quenching applied to homogeneous electrodes using a dead-layer model [19,20]. Nevertheless, the PL quenching to  $\sim 655$  nm suggests, using AES/sputter etch data and eq [1], that the EEF in this sample can separate  $e^-h^+$  pairs at depths of up to  $\sim 0.1$   $\mu\text{m}$  from the surface.

A similar estimate of thickness of the EEF comes from "backside" experiments. Figure 5 presents the companion experiment to Figure 4: the same CdS/Se electrode is excited and its PL viewed from the CdS side using 570-nm excitation. Between open circuit and -0.3V vs. SCE, PL quenching is again absent for  $\lambda \leq 655$  nm, corresponding to disappearance of the EEF at  $\sim 0.1$   $\mu\text{m}$  from the  $\text{CdS}_{0.2}\text{Se}_{0.8}$  surface. Other "backside" excitation wavelengths such as 600 nm, although yielding different PL spectral distributions, also evince a loss of PL quenching at  $\lambda \leq 655$  nm. In general, CdS/Se samples yield EEF depths of  $\sim 0.1$ - $0.2$   $\mu\text{m}$ . Interestingly, the range of EEF depths inferred from these experiments is similar to that found for CdSe/S-based PEC's when the electrode possessed a 1- $\mu\text{m}$  thick graded zone[8]. One other feature worth noting in Fig. 5 is the absence of

PL quenching for  $\lambda \geq 750$  nm. As noted above, we do not know the origin of this subband gap PL, but its insensitivity to applied potential suggests that the states responsible for it lie outside of the EEP.

#### EL Properties

Electroluminescence can be obtained from both homogeneous and inhomogeneous  $n\text{-CdS}_x\text{Se}_{1-x}$  electrodes biased cathodically in aqueous, alkaline, peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ) solutions [5-8]. A number of n-type semiconductors have yielded EL when used as dark cathodes in this medium with the key mechanistic step proposed to be hole injection into the semiconductor's valence band by an intermediate,  $\text{SO}_4^-$  [21-24]. In direct comparisons of EL and PL spectra of homogeneous  $n\text{-CdS}_x\text{Se}_{1-x}$  electrodes, the two spectral distributions are very similar with modest differences attributable to self-absorption effects [5,6].

An EL spectrum for a typical CdS/Se electrode, obtained using a pulse technique [23], is shown in Fig. 6. With  $\lambda_{\text{max}} \sim 660$  nm and a fwhm value of  $\sim 40$  nm, the spectrum closely resembles its PL counterpart (457.9-nm, "frontside" excitation and viewing) and indicates that radiative recombination is confined to within  $\sim 0.2 \mu\text{m}$  of the electrode surface. Surprisingly, there is very little dependence of the spectral distribution on the potential used to initiate EL. Our surprise derives from the CdSe/S system which, as noted in the introduction, exhibits a strongly potential-dependent spectrum with radiative recombination occurring from as deep as  $\sim 1 \mu\text{m}$  from the electrode surface. We rationalize this difference in EL properties for CdSe/Se and CdSe/S, as we did for their PL properties, in terms of the directions of the band gap gradients of the two systems. Also present in Fig. 6 is subband gap EL. Although such emission may contain contributions from transitions involving surface states [21-24], its presence in the PL spectrum of this sample suggests that it arises primarily from bulk intraband gap states.

#### Display Device Applications.

With the continuing interest in the development of novel or improved display devices, particularly multicolored, flat-plate systems [25], we feel it is appropriate to point out that graded materials have characteristics which may prove useful in display technology. One such feature of graded systems is the

ability to emit light of a wide range of colors from the same electrode. For example, graded materials made with a full range of  $\text{CdS}_x\text{Se}_{1-x}$  compositions can emit from the green of CdS to the deep red of CdSe. Such graded electrodes can be utilized in at least two ways. First, as noted previously [8], the color of EL from CdSe/S systems is tunable with modest differences in applied potential. While the CdS/Se samples discussed in this paper were deficient in this regard, preliminary studies of samples with thinner graded zones are more promising.

A second strategy for exploiting the graded systems is through spatially-controlled etching. As shown in Figure 7, removal of some or all of the graded zone affords a change in the color of emission from the etched region. By appropriate masking and etching techniques, patterned, multi-colored emitting electrodes are readily fabricated. We have crudely prepared such electrodes from both CdS/Se and CdSe/S substrates by masking a portion of the electrode surface and chemically etching the exposed material with HCl or  $\text{Br}_2$  in water. The etching was done incrementally, and the electrode was used to generate EL between each etching step so that the extent of removal of the graded layer could be inferred from the color of the emission. After removal of the mask with acetone, the electrode displayed two-toned EL.

An alternative to chemical etching of the graded layer is photoelectrochemical etching (PEC etching) in which the semiconductor electrode is irradiated under reverse bias in a cell with a non-stabilizing electrolyte [26]. Upon light absorption, oxidation of the semiconductor surface occurs, followed by dissolution of the products. For CdS and CdSe this involves oxidation of the chalcogenide lattice to yield  $\text{Cd}^{2+}$  and the chalcogen, which may be removed from the surface by reaction or solvation.

PEC etching has been used previously to enhance the luminescence [5] and the current-voltage properties [27] of various semiconductors under a number of different conditions. Our etching experiments were conducted with CdS/Se and

CdSe/S electrodes at 0.0 V vs. SCE in aqueous 5M NaOH electrolyte. The ensuing photodecomposition reaction was reflected in changes in the EL spectrum. For CdS/Se electrodes, PEC etching is advantageous in that the extent of etching can be controlled by excitation wavelength: Because the band gap increases with depth over the graded zone, etching with monochromatic light of energy between  $\sim 1.7$  and 2.4 eV will only proceed until a composition whose band gap roughly matches the photon energy is exposed to the electrolyte; of course, an alternative to monochromatic light is a white light source with an appropriate cutoff filter. One other advantage of PEC etching for both the CdS/Se and CdSe/S electrodes is that multi-colored EL patterns can be generated by projection rather than by physically masking the surface [28].

#### Experimental

##### Materials.

Samples of CdS/Se were prepared from  $\sim 5 \times 5 \times 1$  mm, vapor-grown, single-crystal c-plates of low resistivity n-CdS (Cleveland Crystals, Inc., Cleveland) in a manner entirely analogous to that reported for the synthesis of CdSe/S [8]. Typically, an etched ( $\text{Br}_2/\text{MeOH}$ ) CdS crystal was heated with 2-8 mg of Se in a sealed, evacuated ( $\sim 1$  Torr) quartz tube for 15 min. After cooling, the crystal was sealed with  $\sim 1$  mg Cd in another evacuated ampoule and heated to  $700^\circ\text{C}$  for 30 minutes. The Se and Cd were purchased from Alfa Products, Danvers, Massachusetts; the Se had  $< 10$  ppm and the Cd  $< 1$  ppm metallic impurities.

The resulting CdS/Se samples were mounted as electrodes as previously described [29], except that the samples were not chemically etched prior to mounting. Ohmic contact was established to either one face or to one edge of each crystal with a Ga/In eutectic. The initial appearances of the two faces of each CdS plate - one shiny and one matte, corresponding to the 0001 "Cd-rich" and  $000\bar{1}$  "S-rich" faces, respectively - were retained even after the CdS/Se synthesis. The work reported here utilized electrodes whose shiny, "Cd-rich" side was exposed to the electrolyte.

The graded layer was removed from the matte side of edge-contacted CdS/Se electrodes with a  $\text{Br}_2/\text{H}_2\text{O}$  etch (1:500 v/v) and/or a 50% HCl (aq) etch. Removal of the layer was confirmed by PL or EL from the etched face. During etching, the graded layer of the shiny face was protected by a hardened layer of clear nail polish (Cutex®). This layer was removed with acetone. A similar layer was applied to the etched matte side to prevent electrical contact with the electrolyte during operation of the electrode in a cell. The protective layer was slowly degraded by the electrolytes used and occasional renewal was required.

The preparation of (poly)sulfide and peroxydisulfate solutions has been described earlier [23,29].

#### Sample composition.

The compositional depth profiles of CdS/Se samples were obtained by AES in conjunction with  $\text{Ar}^+$  sputter etching, as reported previously [8]. A Physical Electronics Model 548 Spectrometer with a 3-keV, 30- $\mu\text{A}$  primary electron beam was used, and the spectrometer voltage ramp was multiplexed to cycle sequentially through the Auger peaks for S, Cd and Se at 152,376 and 1315 eV, respectively. In this way a signal for each of the three components was obtained at  $\sim 15$  s intervals during sputter etching. Carbon and oxygen were seen by AES on the surface of all the samples, but largely disappeared within the first 30s of sputtering. An independent check on the depth of the graded region was obtained, as described previously [7], by measuring the depth of a "trench" etched through the center of the sample to the substrate; the depth was measured with a Dektak contacting stylus (Sloan Technology Corp.).

#### Optical Measurements and PL Properties.

Uncorrected PL spectra were obtained with the Aminco-Bowman spectrofluorometer and  $\text{Ar}^+$  laser setup, as previously described [6,8]. An  $\text{Ar}^+$ -pumped dye laser (Coherent Radiation CR-590) with Rhodamine 590 dye (Exciton Chemical Company, Dayton, Ohio) was used for excitation with wavelengths from  $\sim 560$ -620 nm.



PL spectra resulting from excitation of different crystal strata with 457.9-nm light were obtained by incremental removal of surface material through chemical etching with dilute  $\text{Br}_2/\text{H}_2\text{O}$ . Lateral homogeneity of a CdS/Se sample surface was assessed from PL spectra from several small portions of the surface excited by a laser beam masked to  $\sim 0.1 \times 2 \text{ mm}$ .

#### PEC experiments.

PL properties in a PEC were determined in  $1\text{M OH}^-/1\text{M S}^{2-}/(0.01\text{M S})$  (poly)sulfide electrolyte using cells and electrochemical equipment described earlier [6]. Typically, PL spectra of a CdS/Se electrode were taken at various potentials without changing the alignment of the sample in the spectrometer compartment. Open-circuit spectra were taken before and after in-circuit spectra to show reproducibility; some samples exhibited an initial increase in PL intensity after passage of photocurrent, but in subsequent comparisons showed identical before and after open-circuit spectra. Current-voltage curves were also taken in this geometry, but measurement of  $\phi_x$  required the cell to be set up outside of the spectrometer as mentioned previously [29].

Photoaction spectra were obtained using a 300-W tungsten-halogen projector bulb light source monochromatized by a McPherson Model 270 scanning monochromator, as reported previously [8]. A chopper and lock-in detection were employed to improve the signal-to-noise ratio. An Ithaco (Ithaca, N.Y.) Model 382A chopper with a Model 382B speed control unit chopped the exciting light at 96Hz, and an Ithaco Dynatrac 391 lock-in voltmeter processed the output signal (proportional to the cell current) from the potentiostat.

#### EL spectra.

Uncorrected EL spectra were obtained in alkaline, peroxydisulfate electrolyte ( $5\text{M NaOH}/0.1\text{M K}_2\text{S}_2\text{O}_8$ ) by pulsing the electrode between 0.0V (3 sec) and a potential cathodic of -1.0V (1 sec) vs. SCE, while slowly scanning the emission monochromator (30 nm/min), as described previously [6].

### Pattern Etching.

Chemical etching of patterns onto electrode surfaces was done with a saturated aqueous solution of  $\text{Br}_2$ . After first masking with nail polish the portion of the electrode which was to remain unetched, the electrode was immersed in the etching solution for periods of from 10 s to several minutes, depending on the depth of etch desired. The polish was removed with acetone before operation as an EL electrode. PEC etching was carried out in a well-stirred glass cell containing aqueous 5M NaOH, using a typical three-electrode setup with a saturated calomel electrode (SCE) reference and a Pt foil counterelectrode ( $\sim 7 \times 30$  mm). The semiconductor electrode was held at 0.0V vs. SCE with a PAR Model 173 potentiostat. A variety of light sources including a desk lamp, slide projector (colored light obtained with Corning cut-off filters, nos. 3-66, 2-60, and 2-62), Hg lamp lines (isolated by interference filters), and  $\text{Ar}^+$  laser lines were used. Patterns were etched on electrode surfaces by either physically masking with nail polish and/or electrical tape the portions of the surface to remain unetched, or by merely projecting the desired pattern on the crystal surface. The latter method involved shining either an expanded laser beam or slide projector through a patterned mask onto the electrode face which served as a screen. A convenient method for control of projection PEC etching was to conduct it in the same electrolyte used for EL experiments ( $5\text{M OH}^-/0.1\text{M S}_2\text{O}_8^{2-}$ ). Since EL from an electrode could be generated with the same electrochemical setup used for the PEC etch, the extent of the etch could be periodically monitored by interrupting the light source and pulsing the electrode cathodically to generate EL. PEC etching could then be resumed without disturbing the alignment of the electrode with respect to the projected image.

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## Figure Captions

Fig. 1. Auger/depth profile analysis of a graded CdS/Se sample prepared as described in the text. Argon ion sputter etching was conducted at a rate of  $\sim 300$  Å/min. Se was monitored at five times the sensitivity used for Cd and S detection. C and O were seen as contaminants at sputtering times of  $< 30$  s.

Fig. 2. Uncorrected PL spectra of a graded CdS/Se sample prepared as described in the text. All spectra were obtained in air with 457.9-nm excitation. Curve 1 is the PL spectrum of the as-grown sample and curves 2-4 are spectra obtained after successive chemical etchings with  $\text{Br}_2/\text{H}_2\text{O}$  solutions.

The  $\sim 0.3\text{-cm}^2$  exposed surface area of the sample was uniformly irradiated with  $\sim 1.5$  mW of power, and the excitation geometry was made as nearly identical as possible throughout the experiment.

Fig. 3. Photoaction spectra for a PEC employing an edge-contacted graded CdS/Se electrode in an optically transparent  $1\text{M OH}^-/1\text{M S}^{2-}$  electrolyte; the electrode was held at  $-0.3\text{V}$  vs. SCE. The dashed and solid lines represent "frontside" and "backside" illumination, respectively (see text), using the same incident intensity at each wavelength in both experiments. The plotted values of relative photocurrent have been corrected for variation in light intensity as a function of wavelength.

Fig. 4. PL spectra and  $i$ - $V$  properties of a graded CdS/Se sample prepared as described in the text. The inset shows  $i$ - $V$  properties obtained with 457.9-nm "frontside" excitation of the electrode ( $\sim 0.25\text{-cm}^2$  exposed surface area) when incorporated in a PEC employing  $1\text{M OH}^-/1\text{M S}^{2-}/0.01\text{M S}$  electrolyte.

A sweep rate of  $10$  mV/s was used and the electrolyte redox potential was  $-0.73$  V vs. SCE. Corresponding, uncorrected PL spectra obtained at open circuit (—) and  $-0.3$  V vs. SCE (---) are shown in the main panel of the figure. Both spectra were taken in identical geometries.

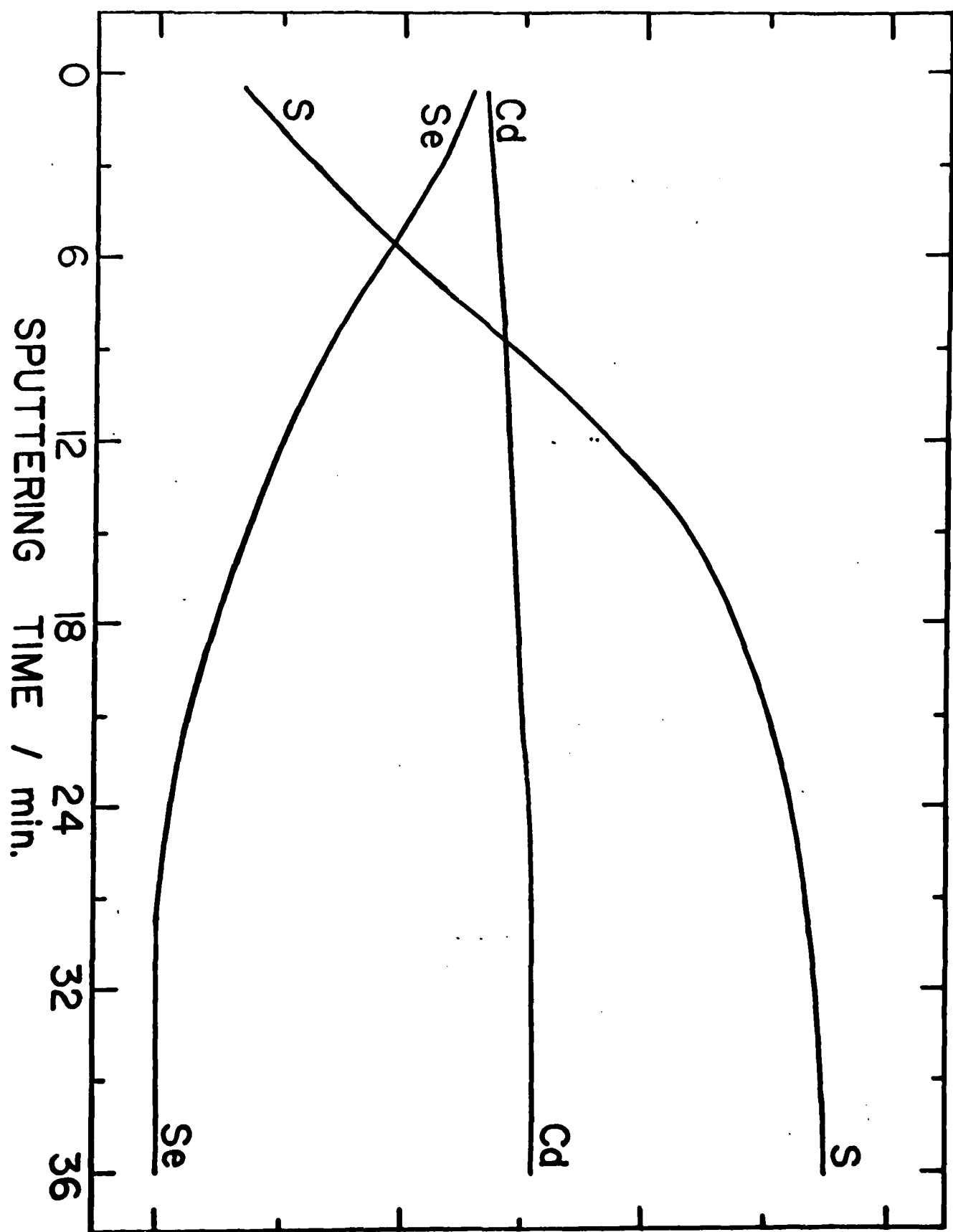
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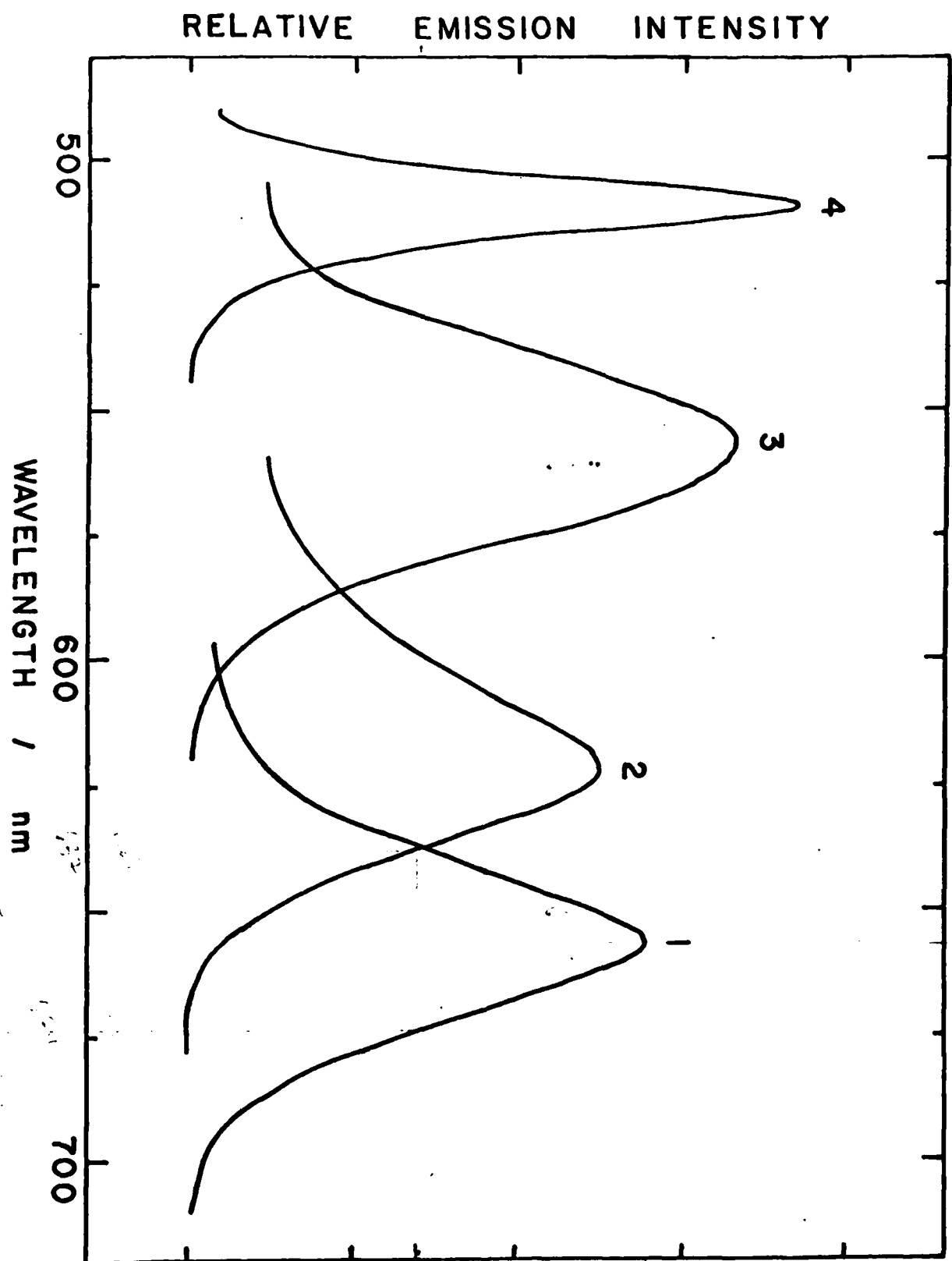
Fig. 5. Uncorrected PL spectra obtained with "backside" illumination and viewing of the same graded CdS/Se electrode as in Fig. 4 in the same PEC. The sample was excited with 570-nm light. The solid curve corresponds to PL obtained at open circuit and the dashed curve to PL at -0.3 V vs. SCE and a current density of  $\sim 0.2 \text{ mA/cm}^2$ . Both spectra were taken in identical geometries. The cut-off filter used to reject excitation light blocked PL at wavelengths  $\leq 600 \text{ nm}$ .

Fig. 6. Uncorrected EL spectrum of a graded CdS/Se sample prepared as described in the text. The series of vertical lines which constitute the EL spectrum were obtained in  $5\text{M OH}^-/0.1\text{M S}_2\text{O}_8^{2-}$  electrolyte by repetitively pulsing between 0.0V (3 sec) and -1.5V vs. SCE (1 sec) while scanning the emission monochromator at 30 nm/min.

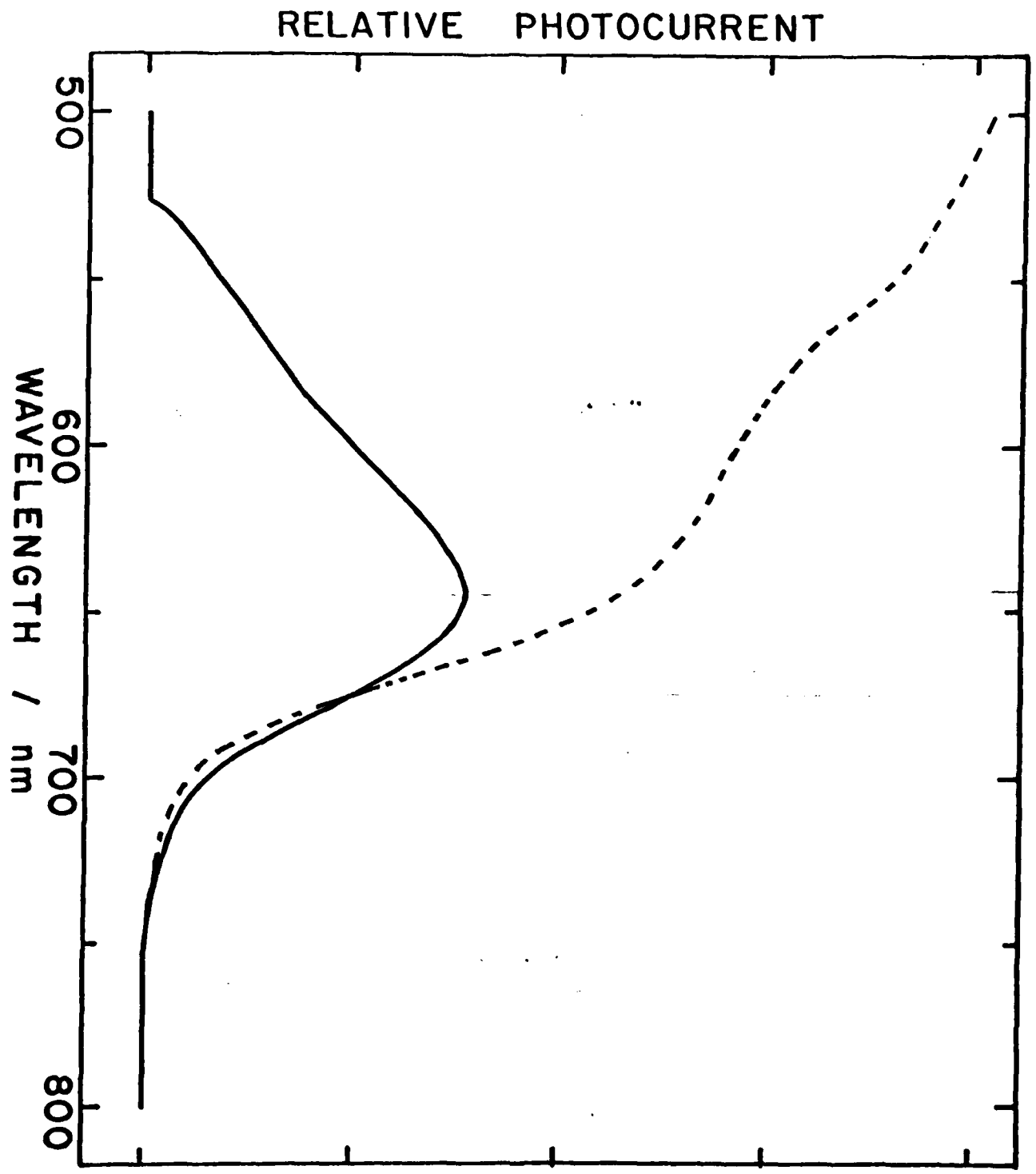
Fig. 7. Schematic of a graded CdS/Se sample etched in a spatially-controlled fashion to yield patterned, multi-colored emission when used as an electrode. The color each exposed composition will emit in an EL experiment is indicated.

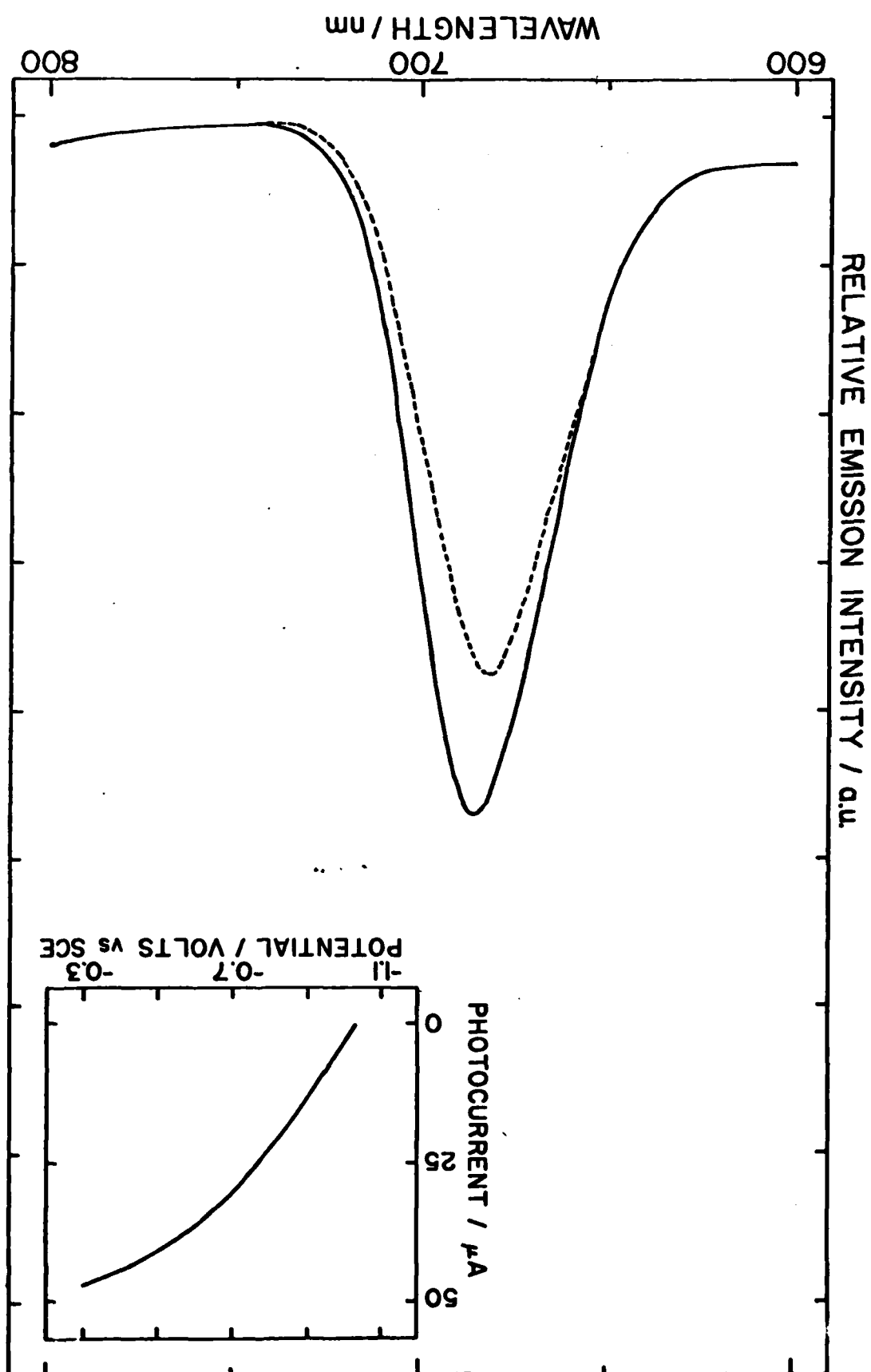
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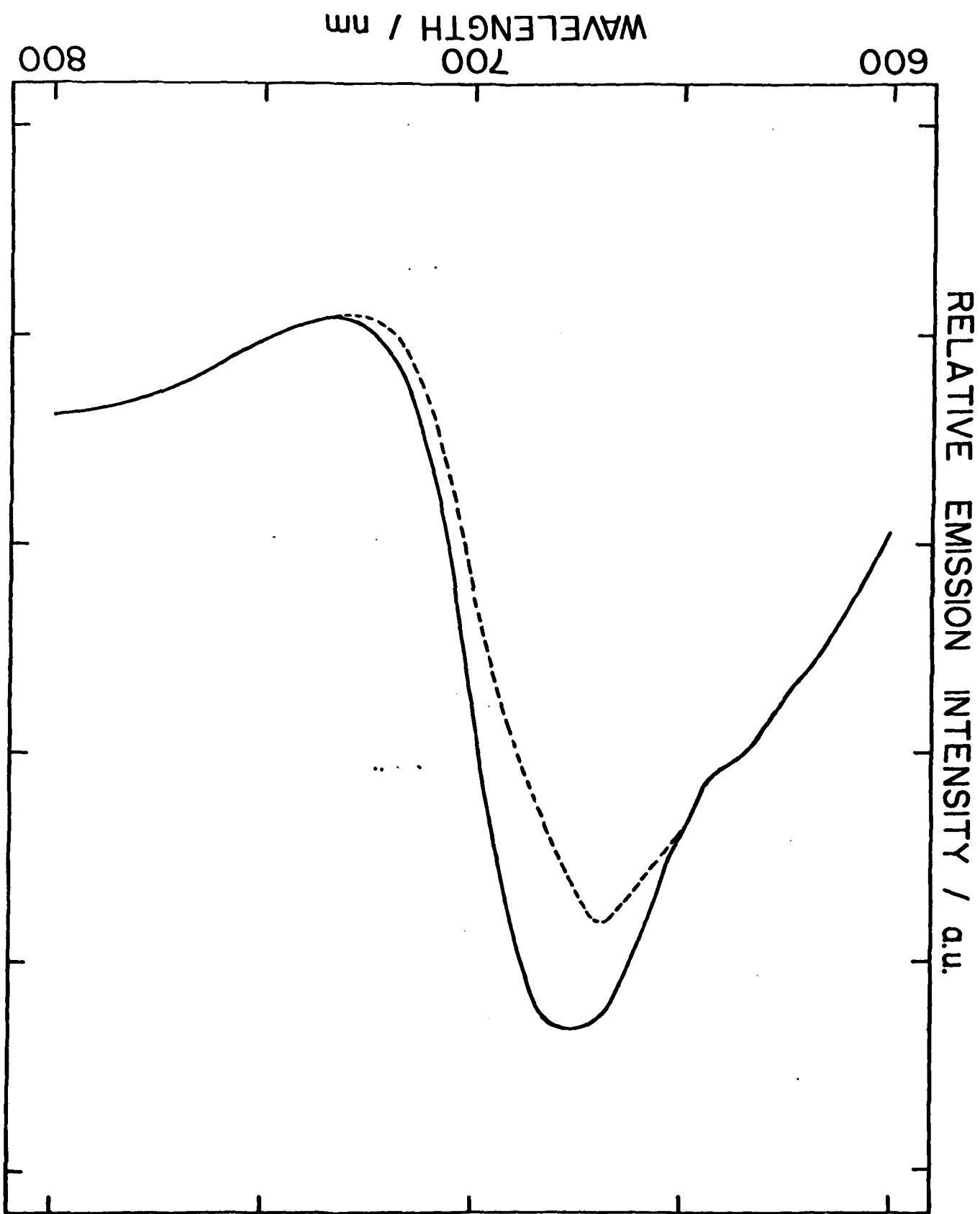


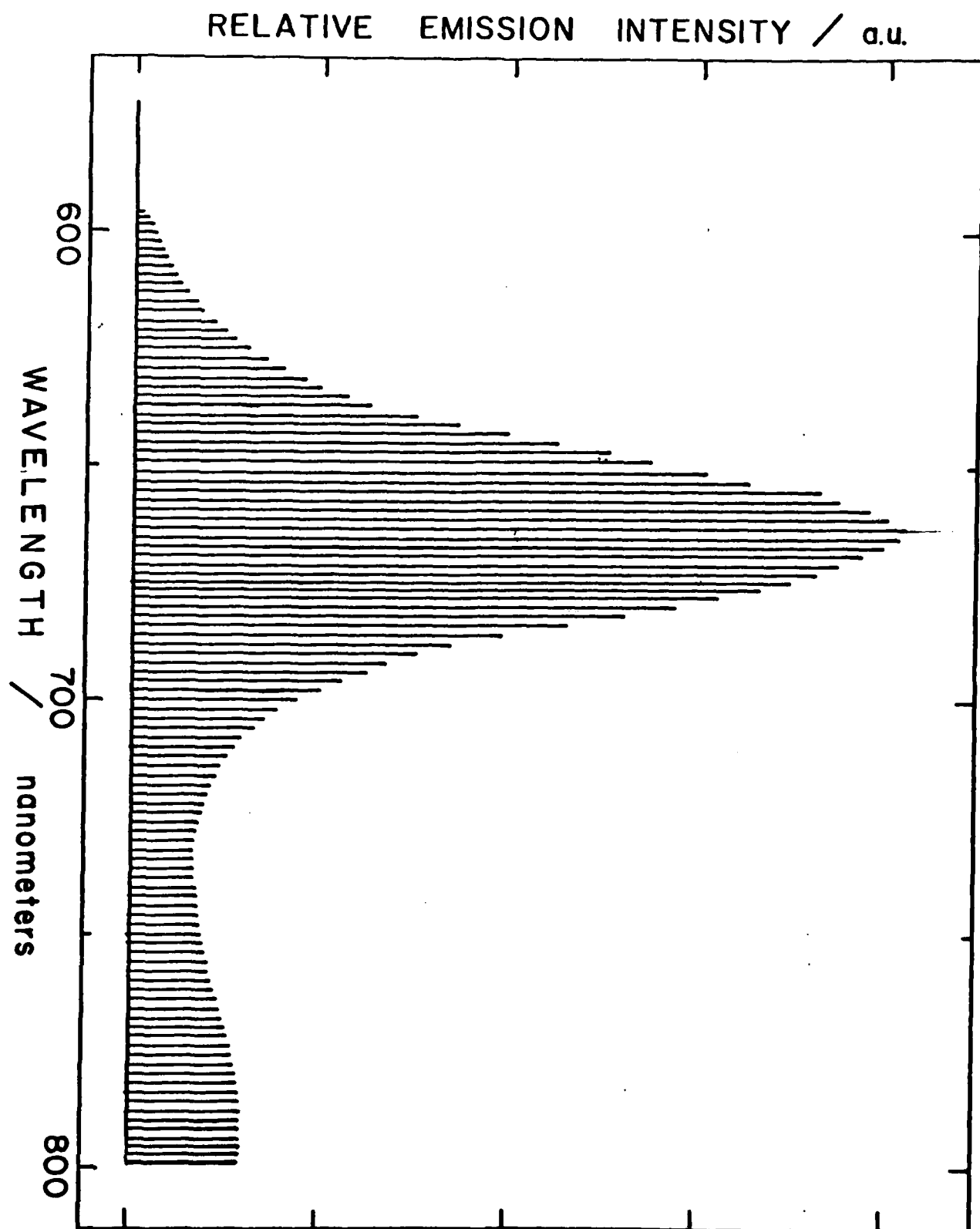




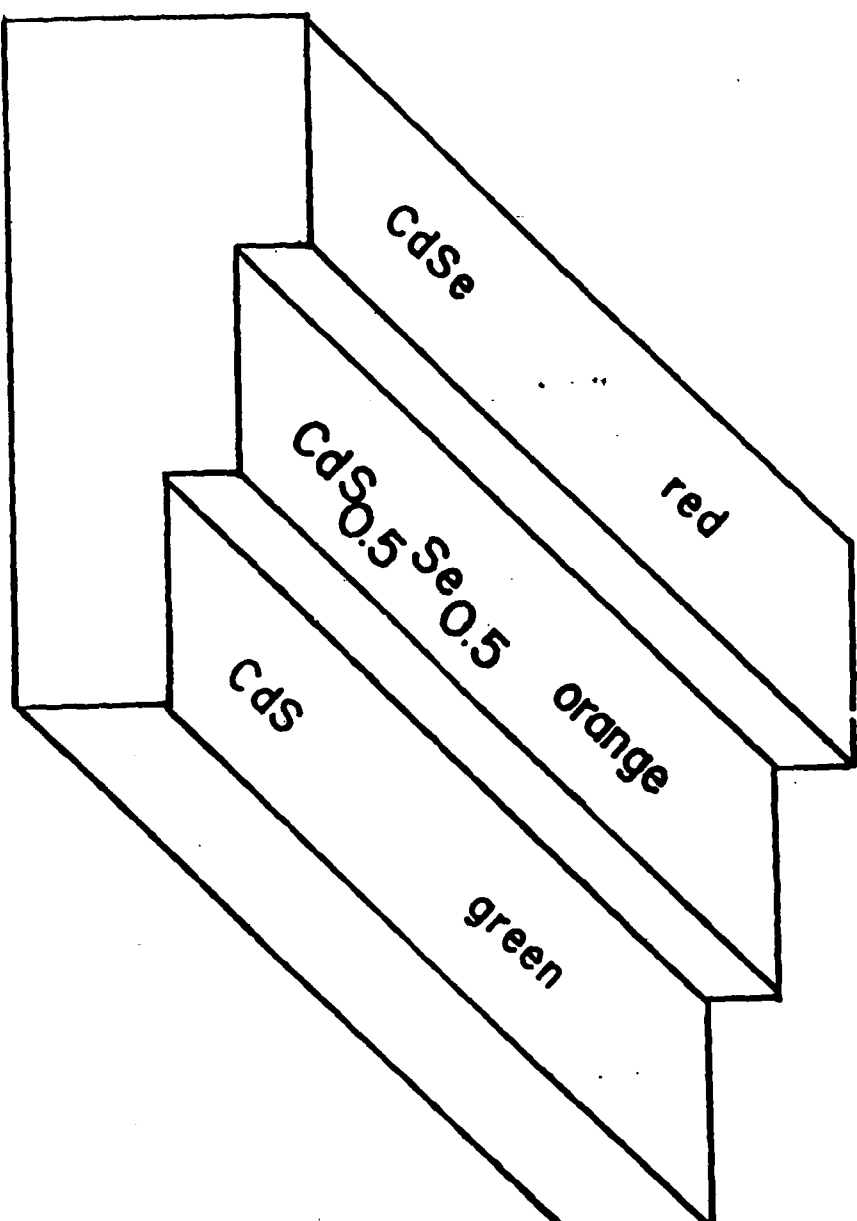








## PATTERNED MULTI-COLORED EMISSION



Samples prepared by spatially-controlled  
chemical etching.

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